PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C22B 34/32, 1/08	A1	(11) International Publication Number: WO 97/46724 (43) International Publication Date: 11 December 1997 (11.12.97)

(21) International Application Number: PCT/CA96/00347

(22) International Filing Date: 31 May 1996 (31.05.96)

(71) Applicant *(for all designated States except US)*: UG PLUS INTERNATIONAL INC. [CA/CA]; 550 Chambly, Sherbrooke, Quebec J1J 2Y2 (CA).

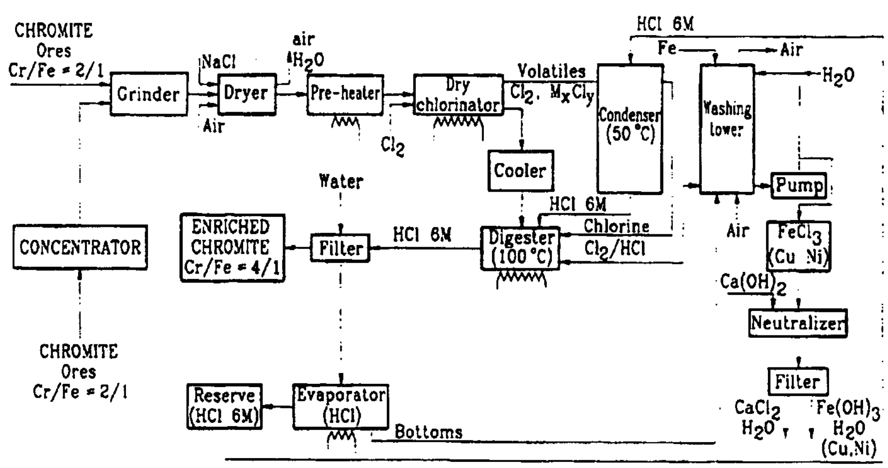
(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: LALANCETTE, Jean-Marc [CA/CA]; 470 Irène-Couture, Sherbrooke, Quebec J1L 1J4 (CA). BERGERON, Mario [CA/CA]; 1253 de Fenouillet, Cap-Rouge, Quebec G1Y 2Y6 (CA). BOSSE, François [CA/CA]; 155 Frédérick Hébert, Rouyn-Noranda, Quebec J9X 1V8 (CA). CLERK, Cyril [CA/CA]; 390 Chemin des Patriotes, North, Mont-St.-Hilaire, Quebec J3H 3H6 (CA).

(74) Agents: DUBUC, Jean et al.; Goudreau Gage Dubuc & Martineau Walker, The Stock Exchange Tower, Suite 3400, 800 Square Victoria, P.O. Box 242, Montreal, Quebec H4Z 1E9 (CA).

(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: PROCESS FOR OBTAINING CHROMIUM ENRICHED CHROMITE FROM CHROMITE ORES



(57) Abstract

A process for obtaining chromium enriched chromite from chromite ores comprising the steps of: dry chlorinating the ores at a temperature between 400 °C and 750 °C to produce a chlorinated substrate containing acid soluble ferric oxide, acid soluble ferric chloride and acid insoluble chromium enriched chromite; digesting the chlorinated substrate with hydrochloric acid to dissolve the ferric oxide and the ferric chloride; and recovering the chromium enriched chromite.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

TITLE OF THE INVENTION

Process for obtaining chromium enriched chromite from chromite ores.

FIELD OF THE INVENTION

The present invention relates to a process for obtaining chromium enriched chromite from chromite ores or chromite concentrates.

BACKGROUND OF THE INVENTION

The production of metallic chromium is an important metallurgical process, this metal being an essential component in high performance alloys and in apparatuses exposed to corrosion. The elaboration of elemental chromium is made from the chromium III oxide, Cr_2O_3. If a crude form of chromium is desired, such as in the ferrochrome master alloys, the chromite, $FeO \bullet Cr_2O_3$, which is the most common occurrence of chromium in nature, is directly reduced with carbon in an arc furnace to give an iron-chromium alloy described by the following equation:

$$FeO \bullet Cr_2O_3 + 4C \rightarrow 4CO + Fe + 2Cr$$

On the other hand, in applications where chromium must be of high purity, such as in electrochemical technologies, pure Cr_2O_3 is required as a starting material and the production of the free metal is done by reaction with aluminum as described by the following equation.

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$

This aluminothermic reaction is quite exothermic (130 Kcal/mole) and gives fused alumina as a secondary product. Therefore, the elaboration of chromium III oxide, either as chromite of high chromium content or as purified Cr_2O_3, is an important step in the production of elemental chromium of good quality.

At present, the production of chromium III oxide consists of a rather elaborate process wherein chromite is used as the starting material. The main steps of this process consist in first fusing the chromite in the hearth of a reverbatory furnace with the addition of alkali hydroxide or carbonate and burned lime. In this way, the chromium is transformed into chromate, through the oxiding action of the furnace flame, in the presence of an excess of oxygen. The chromate leached out with water is converted to

dichromate by the addition of acid. After separation of more sparingly soluble compounds, the dichromate is deposited from the concentrated solution in a sufficiently pure state. Pure chromium III oxide is then obtained by reduction with carbon (see H. REMY, Treatise on Inorganic Chemistry, Vol. II, p. 155, Elsevier Publishing Company, 1956).

It will be readily seen that such a complex procedure makes the resulting chromium III oxide an expensive commodity.

SUMMARY OF THE INVENTION

In the course of a study of the recovery of trace amounts of platinum and related metals from chromite (see NaCl applicant's copending international application PCT/CA96/00060 filed January 30, 1996), the inventors have been led to use chlorine as a reagent for the extraction of these precious metals from the chromite. The presence of a trace amount of sodium chloride in the chromite seems to facilitate the reactions. Although chlorine turned out to be a very selective reagent for the recovery of platinoids, leaving

most of the chromite unaltered, the inventors have noted that, by appropriate operating conditions, a significant amount of the iron oxide present in the chromite ($FeO \bullet Cr_2O_3$) in the presence of NaCl could be oxidized to hematite, thus increasing the Cr/Fe ratio in the residual insoluble chromite. This specific action of chlorine on chromite can be described by the following equation:

$$3[FeO \bullet Cr_2O_3] + 1.5Cl_2 \qquad Fe_2O_3 + FeCl_3 + [0.5FeO \bullet Cr_2O_3]$$

Hematite (Fe_2O_3), being readily soluble in hydrochloric acid can be removed by acid washing from the system, along with the acid soluble ferric chloride formed during the chlorination as shown by the following equation:

$$Fe_2O_3(\text{solid}) + 6HCl\ (\text{aqueous}) \rightarrow 2FeCl_3\ (\text{aqueous}) + 3H_2O\ (\text{liquid})$$

This relatively simple procedure, offers an interesting perspective to an easier access either to a chromite enriched in chromium.

The present invention therefore relates to a process for obtaining chromium enriched chromite from

chromite ores or chromite concentrates which comprises the steps of:

- dry chlorinating the ores ore chromite concentrates at a temperature between 400°C and 750°C to a produce chlorinated substrate containing acid soluble ferric oxide, acid soluble ferric chloride and acid insoluble chromium enriched chromite;
- digesting the obtained chlorinated substrate with hydrochloric acid to dissolve the ferric oxide and the ferric chloride; and
- filtering to recover said chromium enriched chromite.

In another form of the invention, the dry chlorinating step is conducted in the presence of sodium chloride.

In one form of the invention, the chromite ores are concentrated by gravimetric classification prior to chlorination.

In another form of the invention, the digesting step is carried out in the presence of heat.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that this detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

IN THE DRAWINGS

Figure 1 is a block diagram illustrating the various steps of one embodiment of the process of the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

One typical chromite ore used with the present invention is that from the Bushveld complex area in South Africa, containing approximatively 10% chromium of 45% chromite wherein the ratio of Cr to Fe is about 2 to 1.

Referring to the diagram, the ore is reduced to an appropriate size by grinding. It will be readily

understood that too coarse a material will prevent access to the material inside the particles and will slow down the reaction. On the other hand, very fine grinding involves significant cost. A value of particles of about 75 microns appears as a practical compromise between reactivity and cost of grinding.

Alternatively, the chromite ore may be upgraded prior to chlorination so as to give an enriched concentrate containing from 30% to 65% of chromium by weight.

This ground material, either ore or concentrate, is then dried to less than 0.1% of free water and heated up to the appropriate temperature for a dry chlorine treatment, sodium chloride being preferably added at this stage. This temperature of dry chlorination has been found to be variable depending on the refractoriness of the ore under treatment. With certain ores, a temperature of 450°C has been sufficient. In other instances, higher temperatures (up to 700°C) have been required to achieve similar recovery. The temperature of dry chlorination is an important factor in

the capacity of treatment of a given apparatus. This temperature must be high enough to ensure the desired reactions while too high a temperature may prove detrimental to the equipment and may induce undesirable reactions with chromite. It has been found that a temperature in the vicinity of 550°C is a preferred value. The ground ore can be heated to the selected temperature prior to contacting with chlorine or heated up in the chlorinator itself.

The hot ore is then introduced in the dry chlorinator, which is kept at the selected temperature, and a slow stream of chlorine or chlorine containing gas is circulated through the mass at constant temperature. It must be noted that the amount of chlorine required is very small and amounts from 1.0 to 1.5 times the combined chlorine in the course of the dry chlorination. The amount of chlorine is relatively negligible, its consumption being related to the amount of reacting chromite and base metals, such as iron, nickel and copper present in the starting ore. As an indicative estimate, it can be said that some of the base metal sulfides (Cu, Ni), up to 50 percent of the iron in the chromite and

less than one-tenth of one percent of the chromium in the chromite, will be converted into the corresponding soluble chlorides. In order to ensure an homogeneous distribution of the chlorine through the reacting mass, the chlorine stream can be diluted by a carrier gas, such as nitrogen for example. The dry chlorination can be achieved on a continuous basis or batch-wise by simple percolation through the mass of the reacting gas or by the fluidization of the reacting bed or by renewal of the surfaces in a rotating kiln. The contacting time required is relatively long (of the order of half an hour to two hours) depending on the nature of the ore, the degree of completion desired, the temperature used and, to some extent, on the granulometry of the ore. For sake of simplicity of an apparatus which operates under rather aggressive conditions (chlorine at 600°C for example), a static bed of appropriate thickness has been found convenient. Since the material to be treated is to be loaded hot, the heating of the dry chlorination reactor has to be just enough to compensate for heat losses of the system.

The volatiles leaving the dry chlorinator are directed to a condensing tower and quenched by a spray of hydrochloric acid at a concentration of 6M. The temperature in this tower is of the order of 50°C and the condensable are collected and carried down by the acid spray.

The solid left in the dry chlorinator after treatment is dumped, after cooling, in a digester containing the acid from the spray in the condensing tower, and is further digested, at 100°C, for one to several hours, the stirring of the mass being ensured by recirculation of the off gases of the condensation tower through the slurry. The off gases from the digester, mostly nitrogen, hydrochloric acid vapors, chlorine and traces of sulfur compounds, are directed back to a gas treatment system after recycling condensed hydrochloric acid to the digester.

The temperature and duration of digestion in hydrochloric acid in the presence of chlorine must be adjusted in such a fashion as to ensure the complete dissolution of the soluble metal compounds. The heat

increases the rate of such reactions, which could proceed nevertheless at room temperature but at a slower rate. For sake of completeness of dissolution as readily as possible of the metal, hot treatment is preferred over cold treatment and a one to several hours of contacting is retained.

Microscopic examination and diffraction analysis confirm the transformation of significant amounts of the ferrous oxide in chromite into hematite. By acid leach in hydrochloric acid, the hematite can be removed while the chromium III oxide is left undissolved. This breakdown of the spinel structure has a weakening effect on the whole crystal which is rendered more friable. The material can be used as such, being an enriched chromium ore because of FeO removal, or it can be further upgraded by taking advantage of the relatively high density of Cr_2O_3 as compared to the residual silicates initially present in the chromite ore. By application of gravimetric separation, a richer concentrate in Cr_2O_3 can be obtained.

In summary, selective oxydation of chromite can lead to the production of hematite (Fe_2O_3), ferric chloride ($FeCl_3$) and chromium III oxide (Cr_2O_3) by rupture of the spinel structure of the starting chromite. Acid leaching by hydrochloric acid can remove selectively the ferric oxide and chloride fraction, giving a significant enrichment in Cr_2O_3 of the insoluble residual chromite which can be further improved by gravimetric classification or appropriate physical separation of the gangue initially found around the chromite crystal.

The solubilization of the iron oxide associated with the spinel structure of the chromite ($FeO \bullet Cr_2O_3$) thus can be achieved to a variable extent, allowing the removal of from five to sixty five percent of the FeO in the starting chromite, giving an enrichment in chromite from a ratio of 2/1 to more than 4/1.

The range of enrichment is a function of temperature, duration of treatment and structure of the starting ore.

The solution separated from the insoluble chromite ore by filtration is directed to a distillation line or concentration apparatus, such as a reverse osmosis system, in order to recycle the hydrochloric acid at a concentration of 6M which corresponds to the azeotropic composition of the HCl-H_2O system. The bottoms of this distillation contain the iron, the chromium and the base metals (Ni, Cu, etc...) that have been dissolved in the course of the digestion of the dry-chlorinated ore. This material is directed to the gas treatment system which also receives the vapors of the digester.

EXPERIMENTAL

EXAMPLE 1

Samples were obtained from the chromite rich UG-2 layer of the Bushveld complex in South Africa. After grinding to 75 microns, a 35 gram portion of the original sample containing 0.4 to 0.6% added NaCl was subjected to a dry chlorination treatment at 560°C for 90 minutes. Before and after the chlorination experiments, solids were investigated by x-rays diffraction, optical

microscopy and scanning electron microscopy (SEM) coupled to an energy dispersive system (EDX).

Before chlorination, the main minerals present were: chromite, 45% with a Cr/Fe of 2/1; plagioclase feldspar, 45%; pyroxene, 10%; sulfides, 0.02%. After the chlorination experiments, the rupture of the spinel structure of the chromite was noted together with partial transformation (about 50%) of the chromite to hematite and Cr_2O_3. These mineralogical modifications were indicated by: 1) a + 0.26° diffraction shift in the x-ray spectrum of FeO • Cr_2O_3 and appearance of a new peak at 33,57°, both peaks being typical of the x-ray spectrums of hematite and Cr_2O_3; 2) SEM observations and EDX analyses of the grains which showed major signs of alterations revealed by the appearance of hematite and Cr_2O_3 crystals; 3) optical microscopy examination of the altered grains where the presence of hematite grains around the rims of the altered chromite grains could be clearly seen.

The inventors also noted that the plagioclase feldspar grains were untouched by the chlorination while

the pyroxene grains showed minimal alteration, these slight alterations being related to the presence, in the starting materials, of phyllosilicates inclusions in the pyroxenes.

EXAMPLE 2

The chlorinated product obtained from Example 1 was washed with 6M hydrochloric acid. In this solution, a series of 35 elements were analysed by ICP-AES. Only iron showed significative removal from the ore by the chlorination process.

From these analysis, it can be seen that after dry chlorination and leaching with hydrochloric acid, the Cr_2O_3 is essentially intact and not dissolved. As to the iron, about 50% of this element is extracted either as the ferric chloride formed during the dry chlorination or by dissolution of the hematite. The Cr/Fe ratio is then increased to about 4/1 in the end product.

EXAMPLE 3

The chromite ore as described in Example 1 was classified in a spiral so as to give concentrates

containing from 30 to 65% Cr_2O_3 by weight. These concentrates, after grinding to 75 microns, were treated as in Example I with similar increases in the Cr/Fe ratio.

Although the invention has been described above with respect with one specific form, it will be evident to a person skilled in the art that it may be modified and refined in various ways. For example, the grinding step may be carried out after the pre-heating step illustrated in the diagram. It is therefore wished to have it understood that the present invention should not be limited in scope, except by the terms of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for obtaining chromium enriched chromite from chromite ores comprising the steps of:

- dry chlorinating said ores at a temperature from 400°C to 750°C to produce a chlorinated substrate containing acid soluble ferric oxide, acid soluble ferric chloride and acid insoluble chromium enriched chromite;

- digesting said chlorinated substrate with hydrochloric acid to dissolve said ferric oxide and said ferric chloride; and

- filtering to recover said chromium enriched chromite.

2. A process as defined in claim 1, further comprising the step of gravimetrically classifying said ores prior to said dry chlorinating step to obtain a chromite concentrate.

3. A process as defined in claim 1 or 2, wherein said digesting step is carried out in the presence of heat.

4. A process as defined in claim 3, wherein said digesting step is conducted in the presence of heat in the order of 100°C.

5. A process as defined in claim 4, wherein gases resulting from said digesting step are directed to a gas treatment system after recycling condensed hydrochloric acid to said digesting step.

6. A process as defined in claim 1 or 2, wherein said dry chlorinating step is conducted in the presence of sodium chloride.

7. A process as defined in claim 6, comprising the step of heating said ores prior to said dry chlorinating step.

8. A process as defined in claim 6 or 7, further comprising the step of drying said ores prior to said dry chlorinating step; said sodium chloride being introduced at said drying step.

9. A process as defined in claim 8, further comprising the step of grinding said chromite ores prior to said drying step.

10. A process as defined in claim 2, further comprising the step of grinding said chromite ores after said classifying step.

11. A process as defined in claim 9 or 10, wherein said chromite ores are ground to a size of about 75 microns.

12. A process as defined in claim 7, comprising the step of cooling said chlorinated substrate prior to said digesting step.

13. A process as defined in claim 1 or 2, wherein said temperature is about 550°C.

14. A process as defined in claim 1 or 2, further comprising the step of distillating a depleted solution resulting from said filtering step to thereby recycle the hydrochloric acid; bottoms of said distillating step being directed to a system for treating vapours from said digesting step.

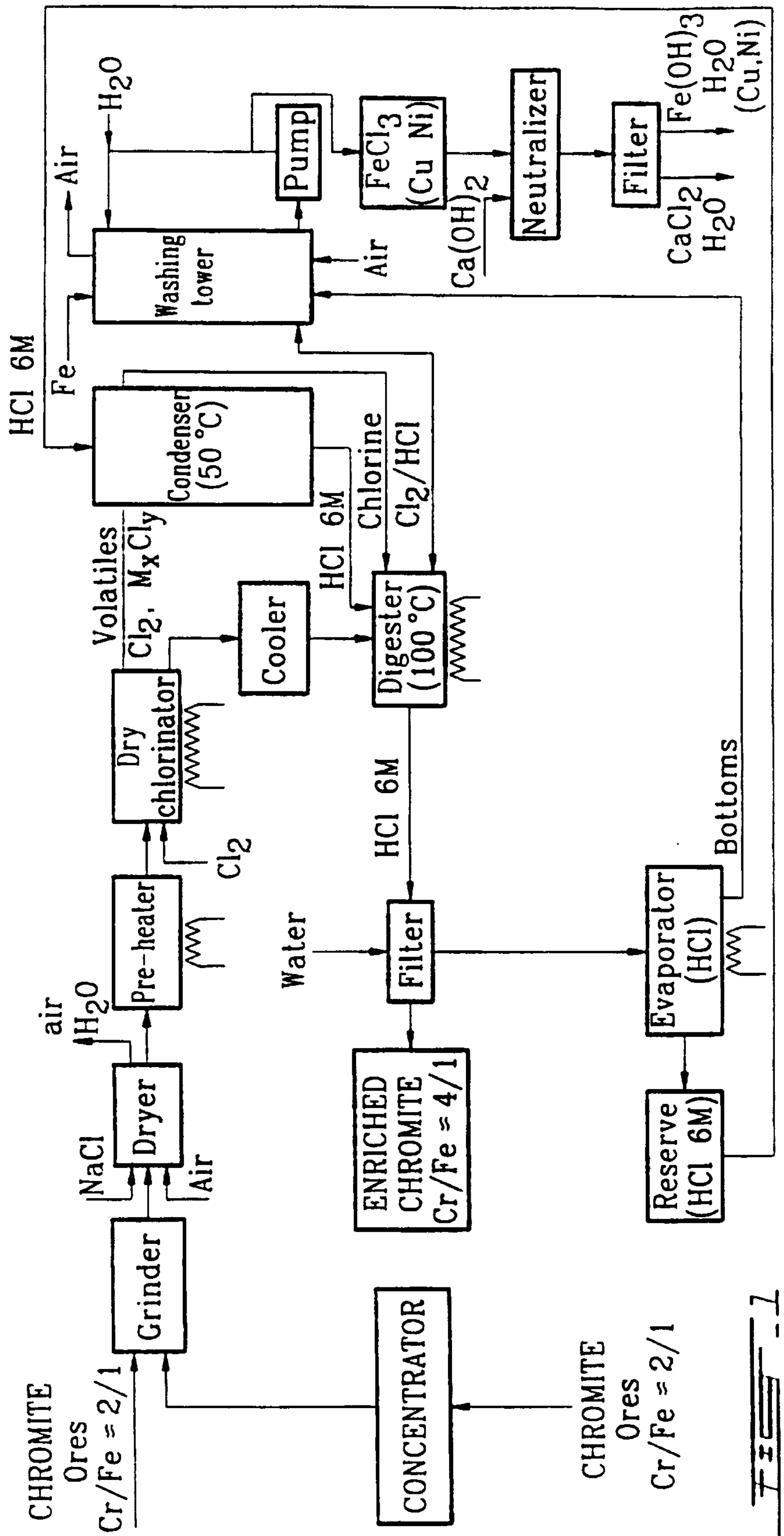

CHROMITE
Ores
Cr/Fe = 2/1
Grinder
NaCl
Air
Dryer
air
H2O
Pre-heater
Cl2
Dry
chlorinator
Volatiles
Cl2, MxCly
Cooler
Condenser
(50 °C)
HCl 6M
Fe
Washing
tower
Air
H2O
Pump
FeCl3
(Cu Ni)
Ca(OH)2
Neutralizer
Filter
CaCl2
H2O
Fe(OH)3
H2O
(Cu,Ni)
HCl 6M
Chlorine
Cl2/HCl
Digester
(100 °C)
HCl 6M
Water
Filter
ENRICHED
CHROMITE
Cr/Fe = 4/1
Evaporator
(HCl)
Bottoms
Reserve
(HCl 6M)
CONCENTRATOR
CHROMITE
Ores
Cr/Fe = 2/1

FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 96/00347

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C22B34/32 C22B1/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 016 516 A (LAPORTE INDUSTRIES LTD.) 1 October 1980 see page 2 - page 3; claims 1,8; example 1 ---	1,2,9-13
A	DE 11 35 668 B (WALTER M. WEIL) 30 August 1962 see claims 1-3 ---	1
A	DE 11 91 971 B (HAALMER CORPORATION) 29 April 1965 see claims 1-4 ---	1,3,4
A	GB 179 201 A (DYSON W.H. ET AL.) 28 July 1921 see claims 1-3; example 6 ---	1
A	BE 644 377 A (UNION CARBIDE CORPORATION) 15 June 1964 ---	1

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
30 January 1997	11. 02. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Bombeke, M

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/LA 96/00347

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 001 042 A (TOYO SODA LTD.) 24 January 1979	
A	US 3 892 639 A (LEAVENWORTH H.W. ET AL.) 1 July 1975	

1

INTERNATIONAL SEARCH REPORT

In. .ation on patent family members

Internatic Application No
PCT/LA 96/00347

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-16516	01-10-80	JP-C-	1507078	13-07-89
		JP-A-	55113849	02-09-80
		JP-B-	63060103	22-11-88
		SE-B-	450132	09-06-87
		SE-A-	8001344	22-08-80
		US-A-	4279640	21-07-81
DE-B-1135668		NONE		
DE-B-1191971		NONE		
GB-A-179201		NONE		
BE-A-644377	15-06-64	NONE		
GB-A-2001042	24-01-79	JP-A-	54018414	10-02-79
		US-A-	4150975	24-04-79
US-A-3892639	01-07-75	NONE		